

U.S. DEPARTMENT OF ENERGY'S (DOE)
VEHICLE TECHNOLOGIES OFFICE (VTO)
2020 ANNUAL MERIT REVIEW (AMR)

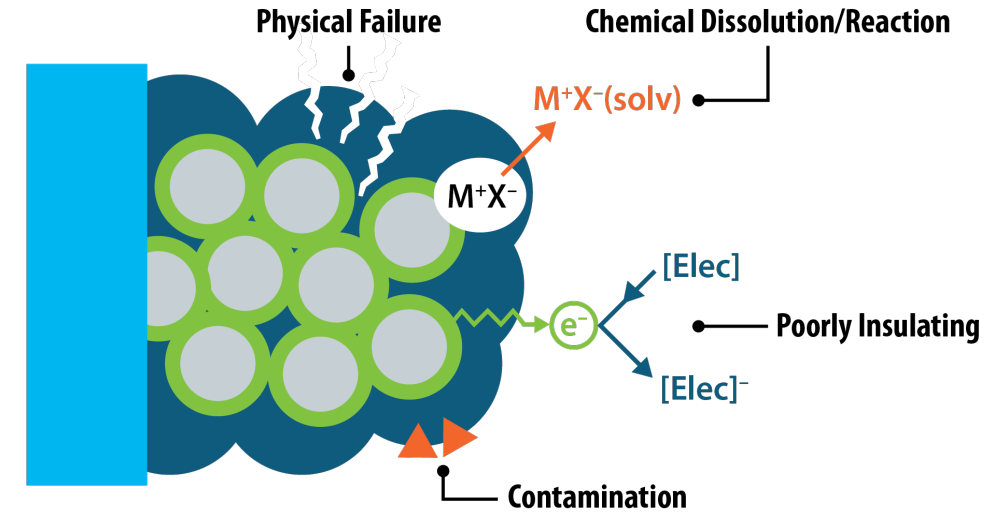
THE SILICON CONSORTIUM PROJECT

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Next-Generation Materials Thrust
NREL

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Project ID: bat498
Poster presentation

OVERVIEW

Timeline

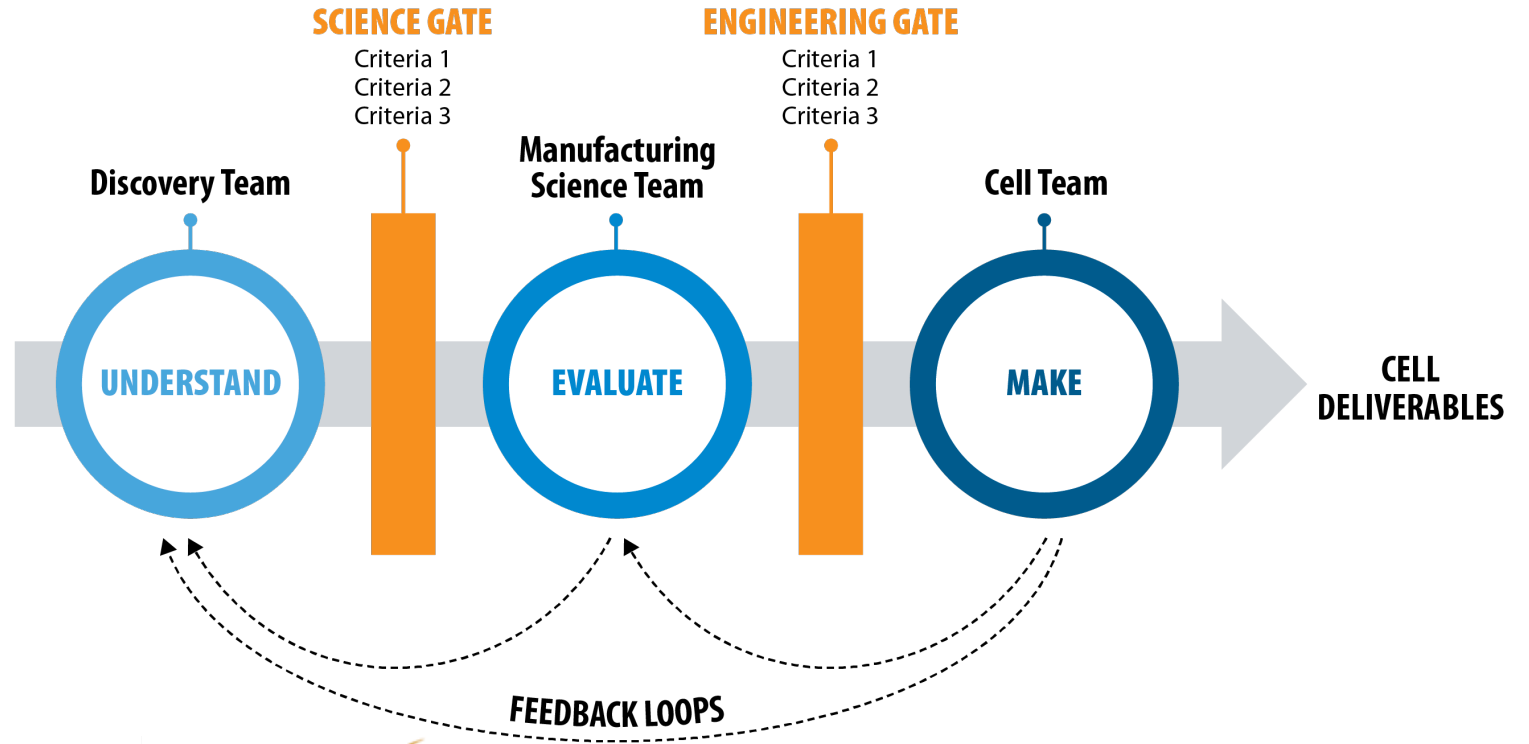
- October 1st 2020 - September 30st 2025.
- Percent complete: 10%

Budget

- Funding for FY20: **\$7500K**

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
 - Cost, Performance and Safety



OUTLINE

Timeline

- October 1st 2020 - September 30st 2025.
- Percent complete: 10%

Budget

- FY2021 funding:
\$7500K

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
- Cost, Performance and Safety

Research Thrusts

- Advanced characterization of the Si/SEI/electrolyte interfaces and interphases
- Electrochemical stability of the SEI
- Mechanical characterization of the SEI
- **Next-generation materials discovery and development**
- The science of manufacturing
- Cell manufacturing

MILESTONES

- Establish a pre-lithiation protocol that can be utilized by all partners Q1 (complete)
- Go/no-go on HF etching of silicon oxide-silicon as viable route to silicon Q2 (complete)
- Go/No go on the Moire interferometry at as a method of probing the calendar life of the silicon SEI? Q3 (complete)
- Produce 20 grams of next generation silicon's with at least two different coatings, at least one of which exhibits enhanced calendar life over the baseline commercial silicon (NREL-centric) Q4 (on schedule)
- Advanced version of the calendar life protocols that quantifies calendar life in silicon-based anodes within 20% of the “real” calendar life predictions of calendar life. Q4 (on schedule)
- Synthesis and testing of 5 different metallic glasses with theoretical capacities > 1000 mAh/g Q4 (on schedule)
- Identify active cell components and cell designs to achieve stable calendar life electrode performance with a cell build demonstrating 300 cycles with <20% capacity fade. Q4 (on schedule)

NEXT-GENERATION MATERIALS

Relevance

Build from SEISta and Si Deep Dive project knowledge base:
Non-engineered Si materials and interfaces exhibit poor cycle and calendar life in Si-based anode electrodes.

Approach

Main approaches to enhancing cycle and calendar life:

1. Electrolyte Formulation
2. Active Material Composition
3. Advanced Design Interfaces

Synergy and Partnership with Other Teams

Rapid feedback on materials modifications:

1. Advanced Characterization of the Si/SEI/electrolyte
2. Electrochemical Stability
3. Mechanical Characterization
4. Science of Manufacturing (processing)

B. Cunningham
bat343

Accomplishment

Approach

Target Metrics for Year 3 Milestone

Electrode level

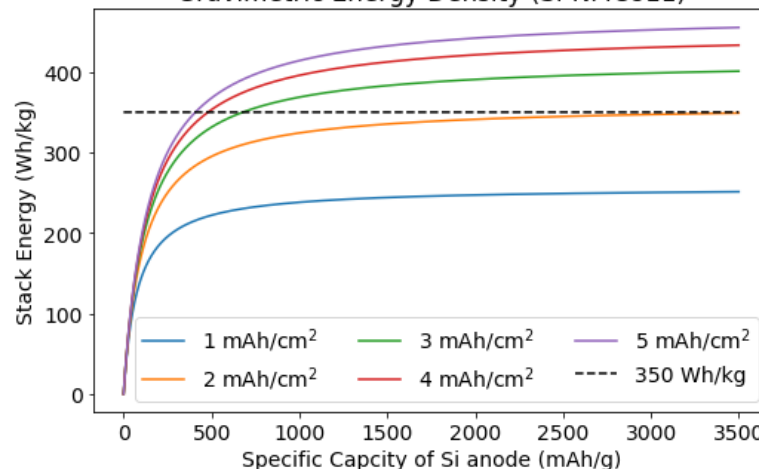
- > 1000 mAh/g
- > 1000 mAh/cm³
- > 3 mAh/cm²
- > 99.98% CE
- < 1.826*10⁻⁵ Amps/Ah Li-consumption

Year 3 Cell level

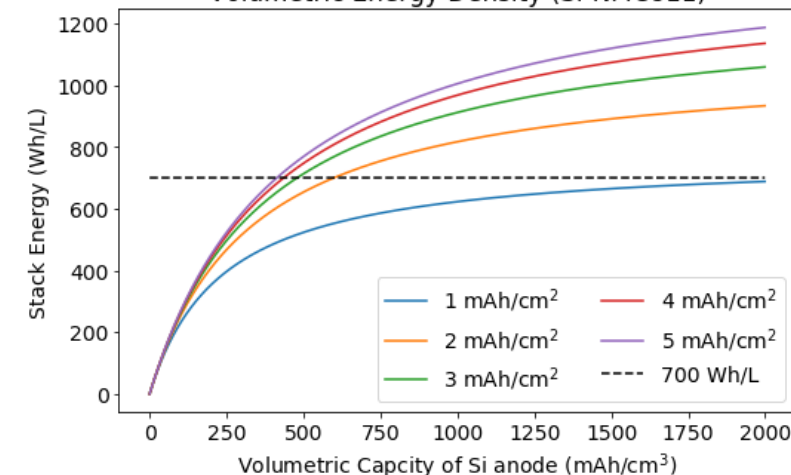
- > 350 Wh/kg
- > 750 Wh/L
- > 5 years
- > 1000 cycles

Model Used to Set Electrode-Level Targets, Guide Development

Gravimetric Energy Density (Si-NMC811)



Volumetric Energy Density (Si-NMC811)



Main take away points:

- Diminishing returns over 1000 mAh/g or mAh/cm³
- Energy more strongly dependent on areal loading
- Likely need ≥3 mAh/cm² to hit milestones

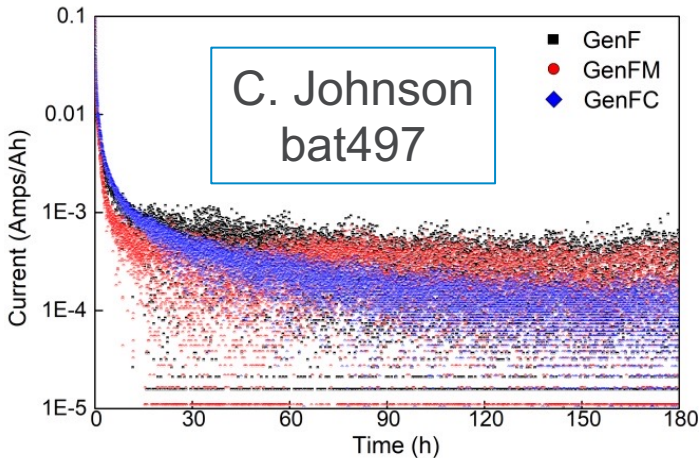
HIGHLIGHT – TERNARY ZINTL PHASES

Accomplishment

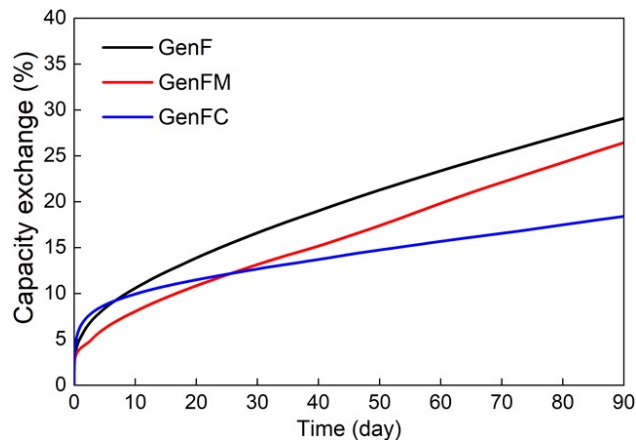
Motivation : Improving Calendar life of Silicon Anodes

Approach: Stabilization Inorganic SEI via Multivalent Electrolyte Additives (0.1 M Mg and Ca TFSI salts)

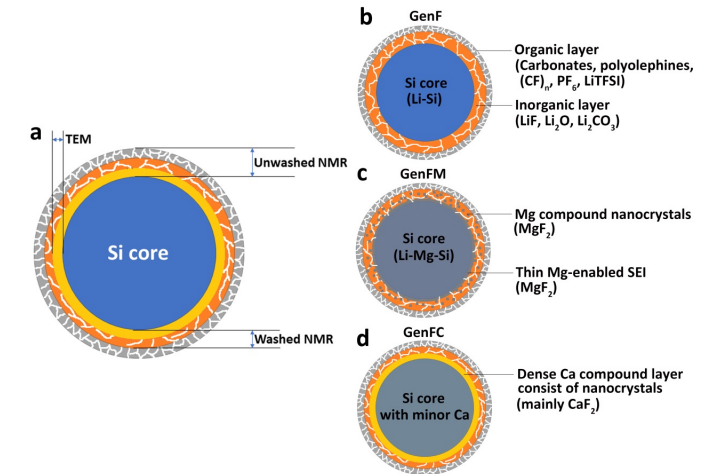
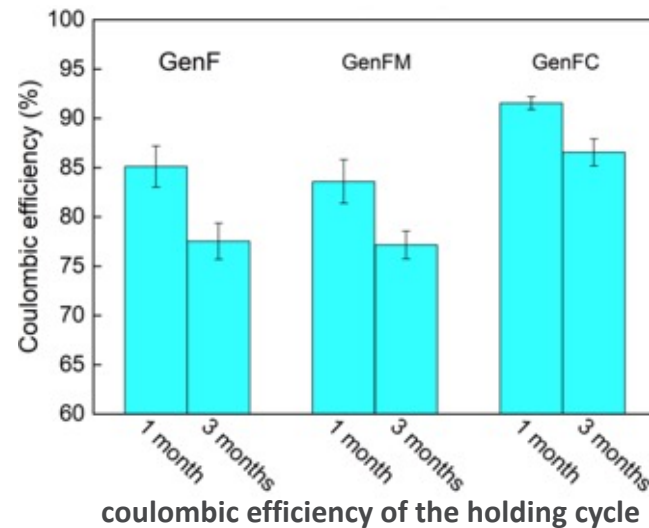
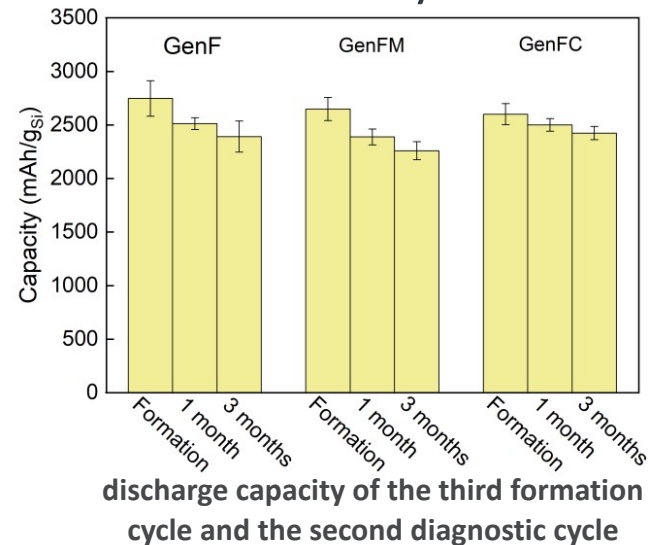
Calendar Lifetime Protocol



leakage current and reversible processes



coulombic efficiency of the holding cycle



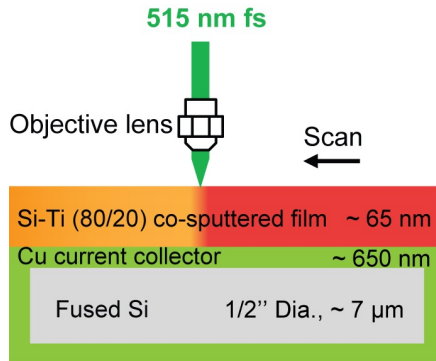
CaF₂ / MgF₂ formation contributes to robust in-situ SEI formation

- Ca additive showed lower current leakage during calendar aging.
- The average capacity decay rate of GenFC after one-month holding was 4.07 % and that after three-month holding was 6.98 % .
- The average coulombic efficiency of GenFC after one-month holding was 91.53 %, and it remained 86.54 % after three-month holding.

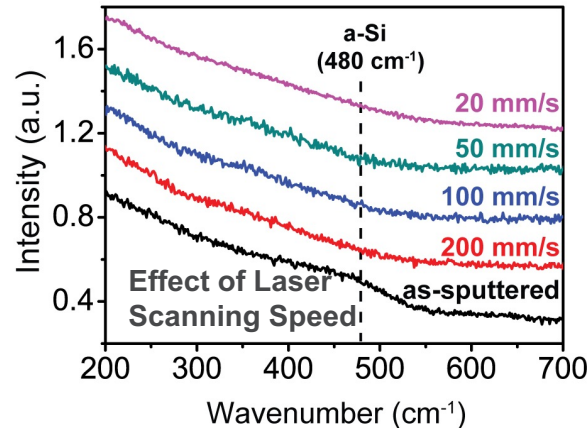
HIGHLIGHT – SILICON ALLOYS VIA ULTRAFAST NONEQUILIBRIUM PROCESSING

Accomplishment

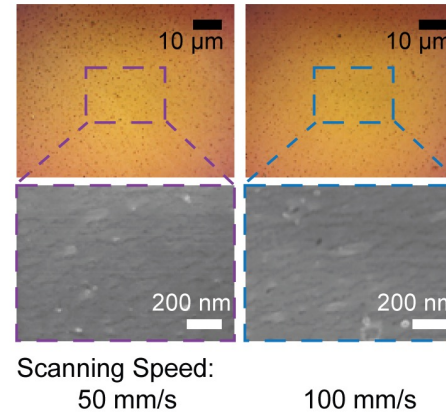
Experimental System



Raman

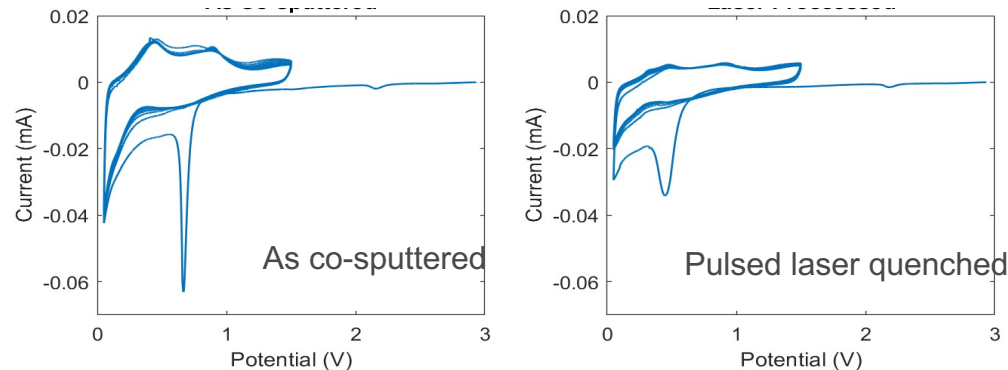


Optical Microscopy & SE



- Laser quenching to form amorphous Si-Ti metallic glasses.
- Raman spectra confirm lack of crystalline phases.
- Successful fabrication of homogeneous laser quenched surfaces.

Cyclic voltammetry



- Si-Ti films electrochemically active both before and after laser quenching.
- Shift in prominent reduction peak during first cathodic sweep; current response after laser quenching may be attributed to partial oxidation of Si-Ti.
- Conclusions: Laser quenching is a facile method to rapidly prepare Si alloy phase space as new Li-ion anodes
- Next step: Laser quenching in Ar or He flow (vs. air).

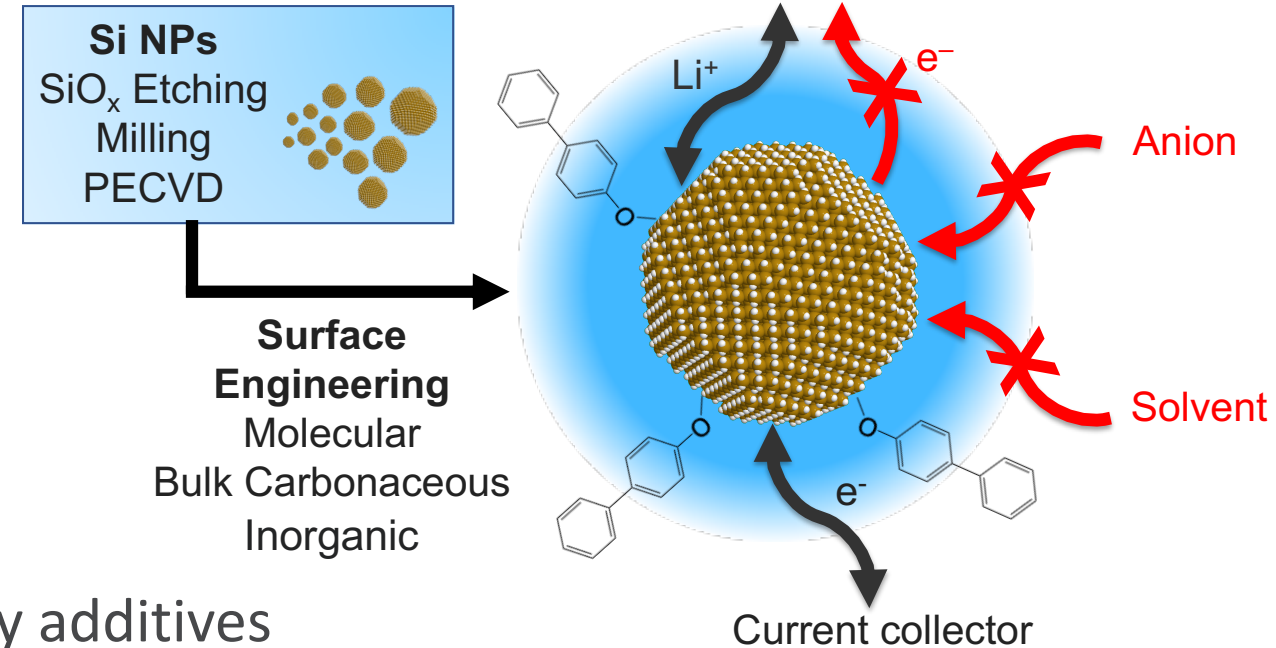
ADVANCED DESIGN INTERFACES

Approach

Interface Engineering as a Strategy to Enhance Calendar Lifetime

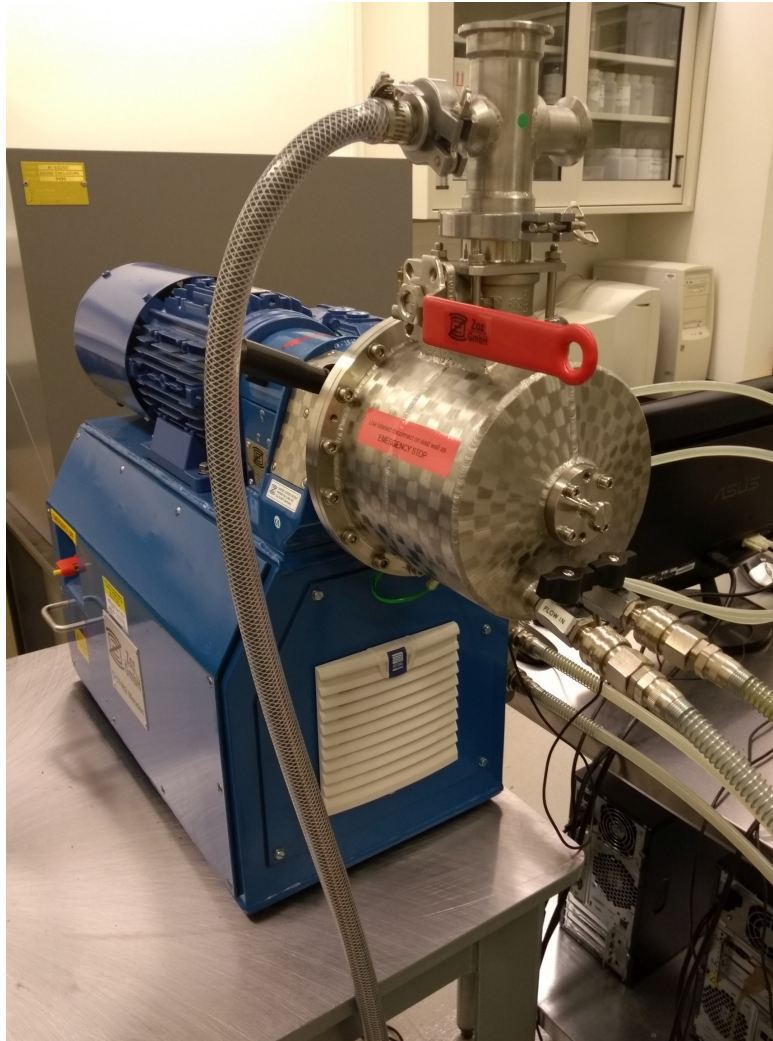
Strategies developed from knowledge obtained in the predecessor SEISta and Si Deep Dive projects

- Design and develop molecular organic and bulk carbonaceous surface coatings
 - Minimize direct Si-electrolyte contact
 - Enhance slurry processability and electrode morphology
- Use SiO_x prelithiation, electrolyte and slurry additives to create inorganic SEI (LiF , Li_xSiO_y , Li_2O , Li_2CO_3 , etc.)
- Understand how the surface chemistry affects SEI growth and dissolution, mass and charge transport across SEI



MILLING IN SACRIFICIAL REAGENTS TO COAT SILICON AND STABILIZE THE INTERFACE

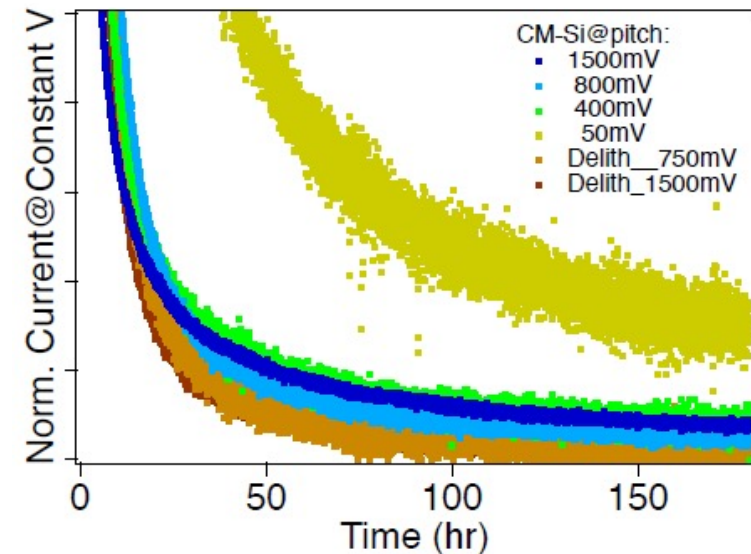
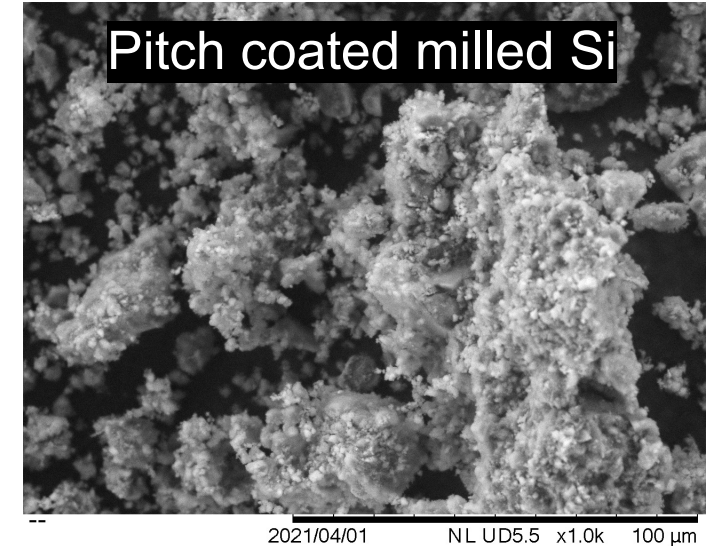
Accomplishment



Identified potentially stable surface functionalization that are stable with cycling

Purposely covalently bond to surface at >200g scale

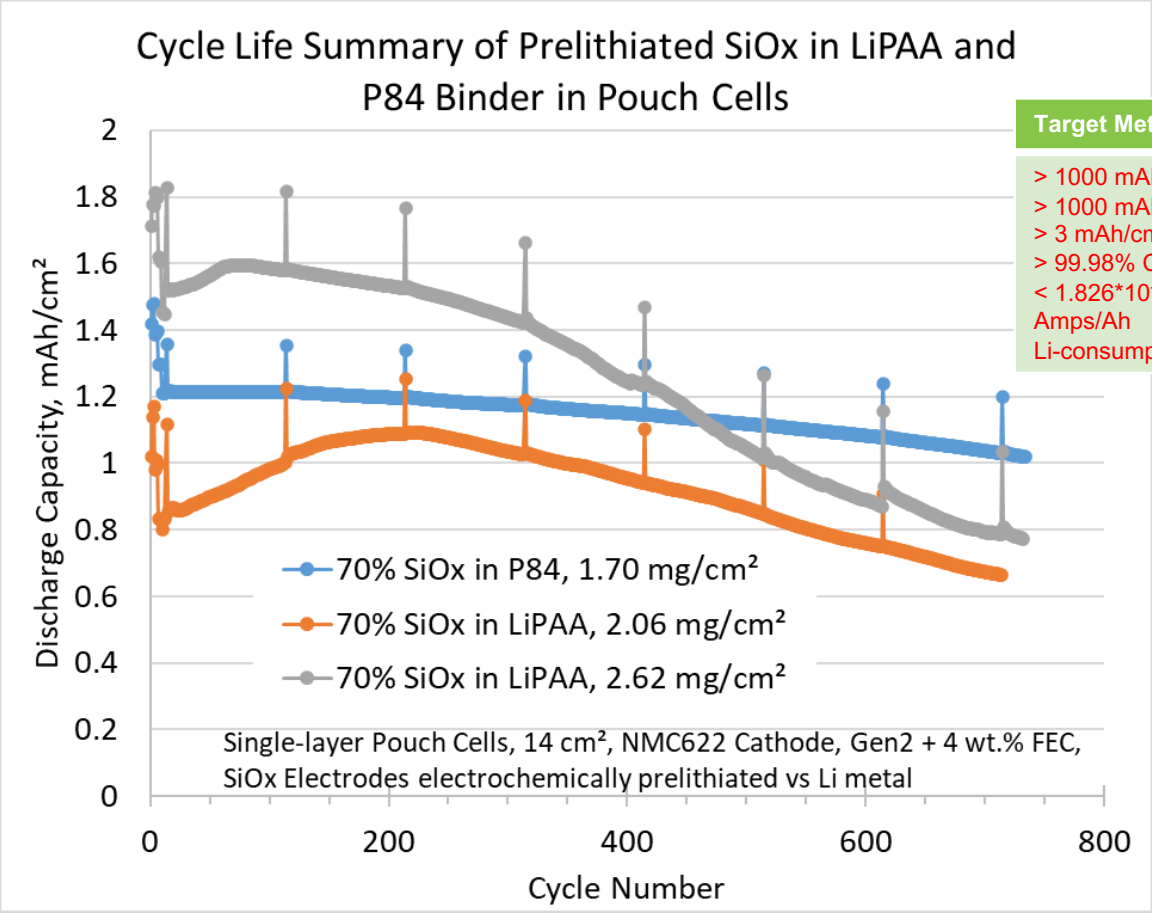
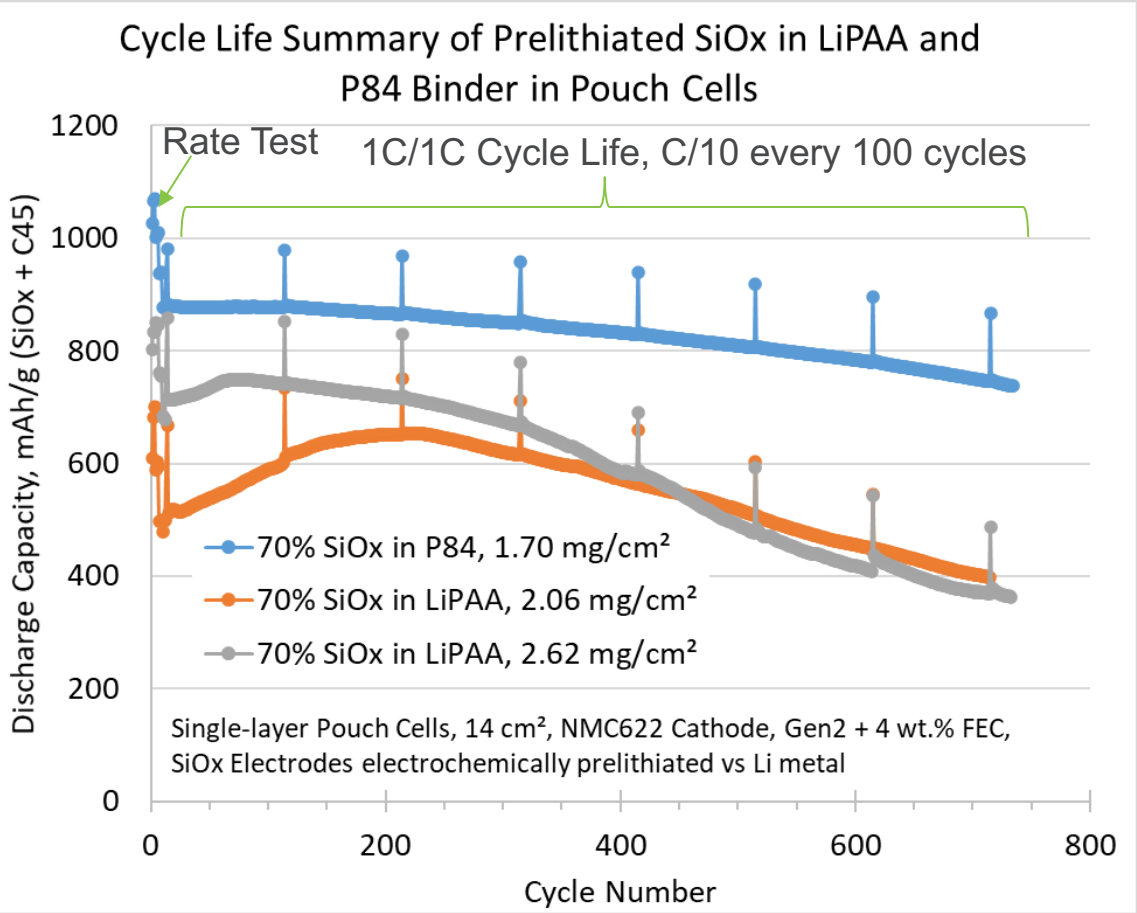
Surface functionalization reduce corrosion currents while enabling extended cycling.



POUCH CELLS WITH PRELITHIATED SiO_x ELECTRODES EXCEED 300 CYCLES WITH NMP AND AQUEOUS BINDERS

Accomplishment

Osaka SiO Summary Data: LiPAA vs polyimide (PI a.k.a. P84)



Next Steps: 1. Use dQ/dV analysis to optimize electrochemical cycling protocol;
2. Increase areal capacity; 3. Screen against new electrolytes

SI@NMP COATING: PAA VS PI

Accomplishment

Electrode fabrication:

- Intrinsic PECVD 5.9 nm Si@SiH_x
- PAA Slurry: 30 Si@NMP : 45 PAA: 15 C45 in NMP
- PI Slurry: 30 Si@NMP : 45 PI : 15 C45 in NMP
- Cycling in Gen2 + 10% FEC Electrolyte

Full-cell cycling:

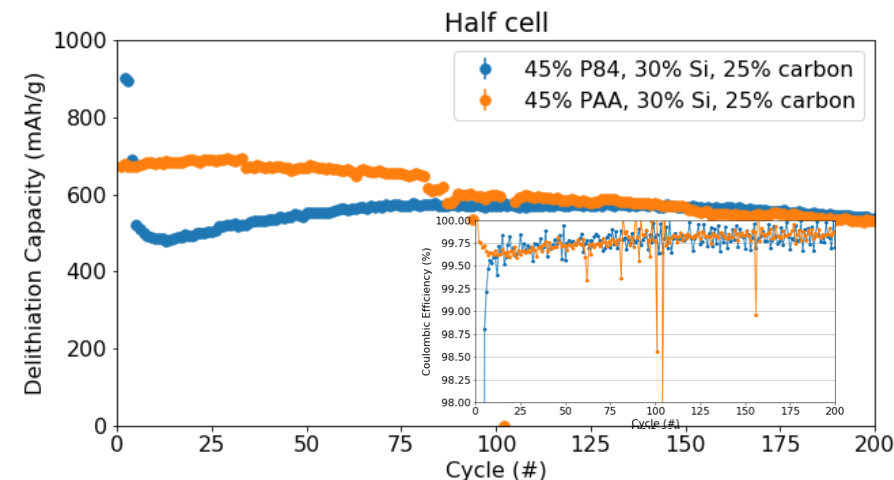
- No prelithiation
- ~1.8 mAh/cm² LFP cathode
- ~0.7 mAh/cm² Si (>150% excess Li-inventory)
- 4x @ C/3, 1x HPPC, 95x @ 1C, repeat (2.7-3.44V)

Target Metrics

> 1000 mAh/g
> 1000 mAh/cm²
> 3 mAh/cm²
> 99.98% CE
< 1.826*10⁻⁵
Amps/Ah
Li-consumption

Half cell

3x C/20 (0.01 – 1.5 V)
then 1C 100x



**Next Steps: 1. Increase Si utilization (porosity);
2. Increase areal capacity; 3. Understand safety**

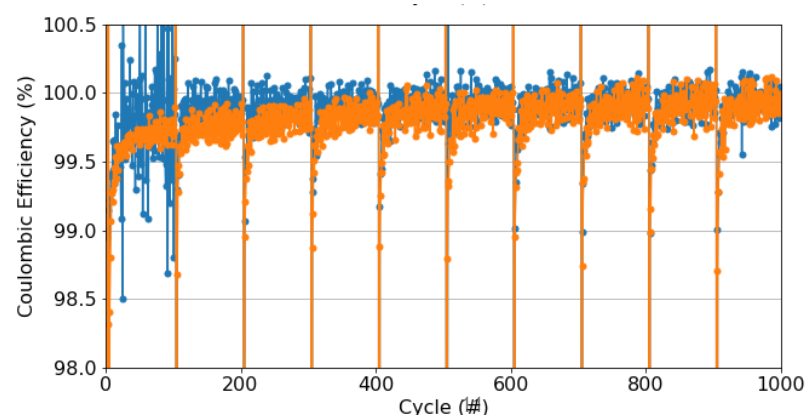
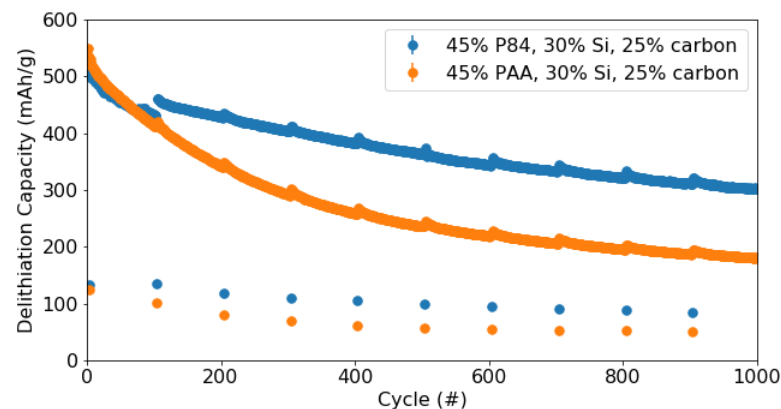
Full cell

PAA

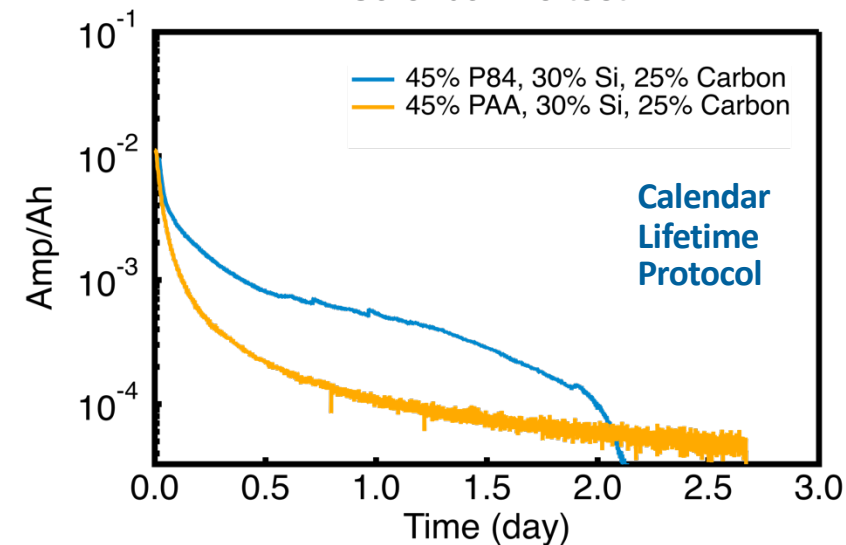
1.32 mAh/cm² @ BOL
vs ~1.5 mAh/cm² NMC622
~32% capacity
retention at cycle 1000 (C/3)

PI

1.42 mAh/cm² @ BOL
vs ~1.5 mAh/cm² NMC622
~60% capacity
retention at cycle 1000 (C/3)



Calendar life test



SI@PITCH: SP² + SP³ CARBON COATING

Accomplishment

Electrode fabrication:

- Intrinsic PECVD 5.9 nm Si@SiH_x
- Pitch coated and carbonized (50:50 Si:pitch)
- Slurry: 8 Si/pitch : 1 Timcal C65 : 1 P84 in NMP
- Cycling in Gen2 + 10% FEC Electrolyte

Full-cell cycling:

- Formed in half-cell: 3x C/20, 1x C/3 (10-750 mV vs. Li)
- ~1.8 mAh/cm² LFP cathode
- ~0.8 mAh/cm² Si/pitch anode
- 4x @ C/3, 1x HPPC, 95x @ 1C, repeat (2.7-3.44V)

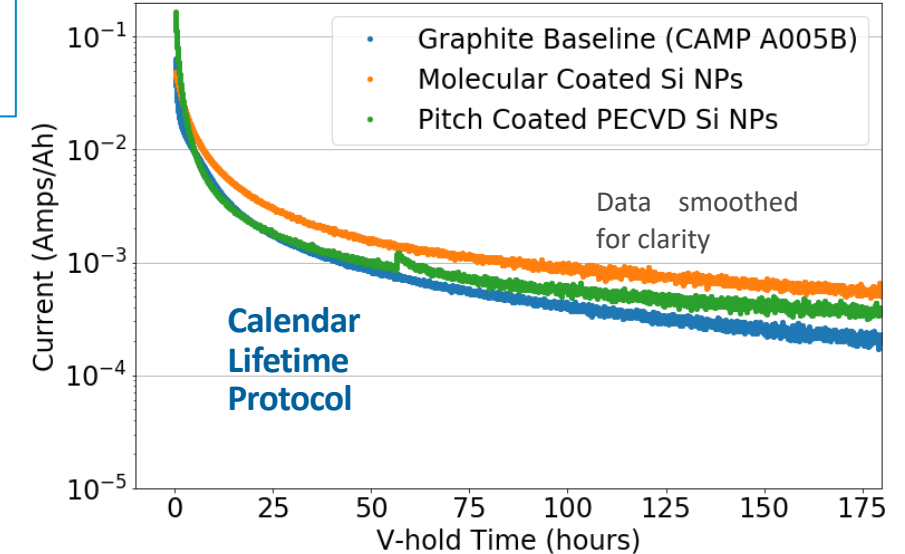
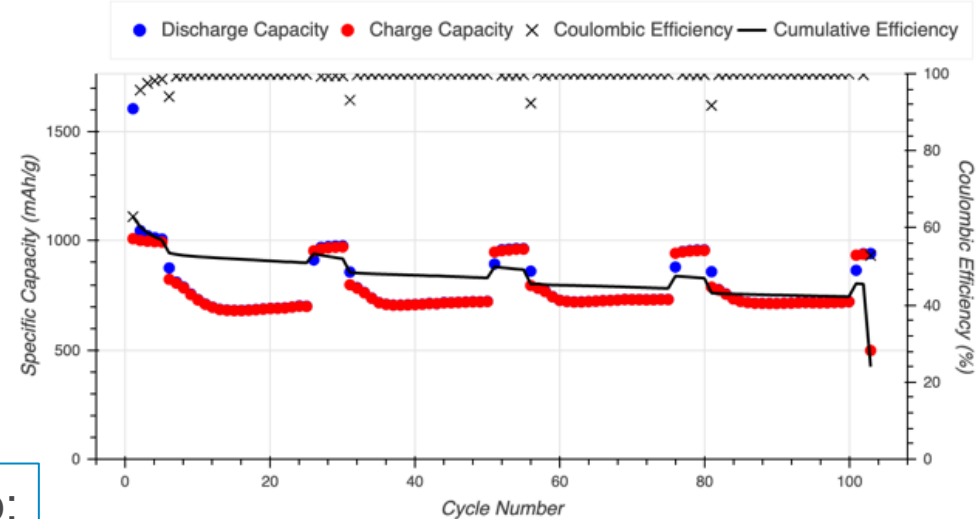
Half cell

5x @ C/20, 20x @ C/3, repeat (0.01-0.75V)

Target Metrics

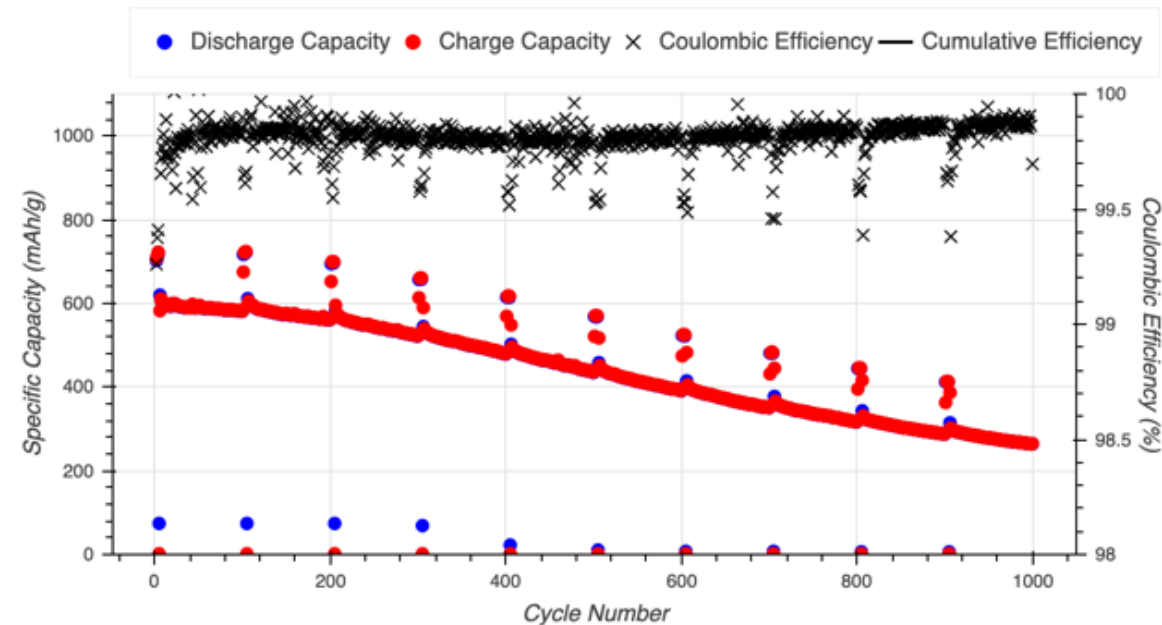
> 1000 mAh/g
> 1000 mAh/cm³
> 3 mAh/cm²
> 99.98% CE
< 1.826*10⁻⁵ Amps/Ah
Li-consumption

Scale-up:
G. Veith
bat500



Full cell

~0.8 mAh/cm² @ BOL
vs ~1.8 mAh/cm² LFP
~80% capacity retention at cycle 500 (@ C/3)



Next Steps: 1. Understand porosity; 2. Increase areal capacity; 3. Alternative coatings

B-DOPED SI@LI SALT COATING

Accomplishment

Electrode fabrication:

- Boron-doped PECVD 6.5 nm B:Si@SiH_x
- Slurry: 51% B:Si : 10% SWCNTs-COOH : 31% PAA : 8% Li-Acrylate in NMP or 55% Si : 5% SWCNTs-COOH : 30% PAA : 10% Li-Carbonate
- Cycling in Gen2 + 10% FEC Electrolyte

Full-cell cycling:

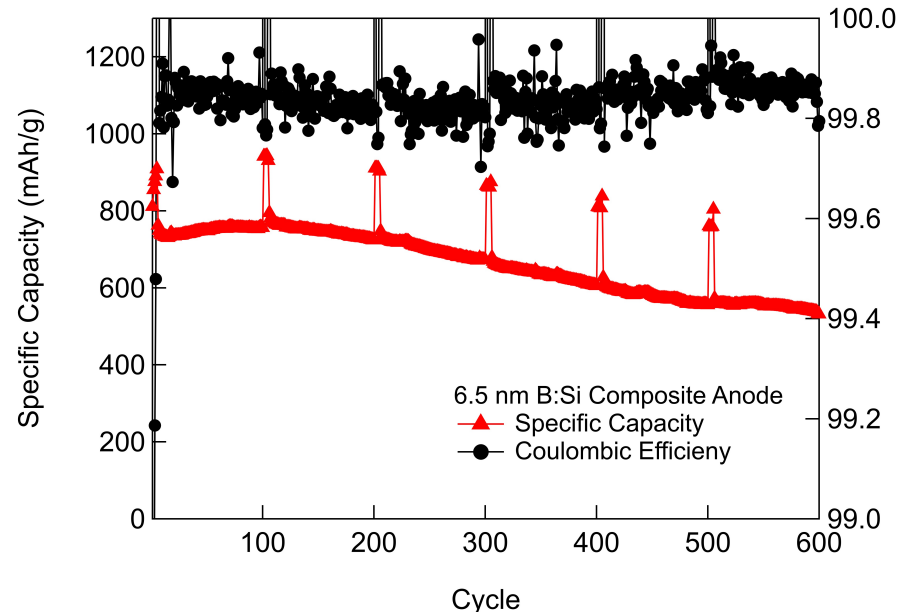
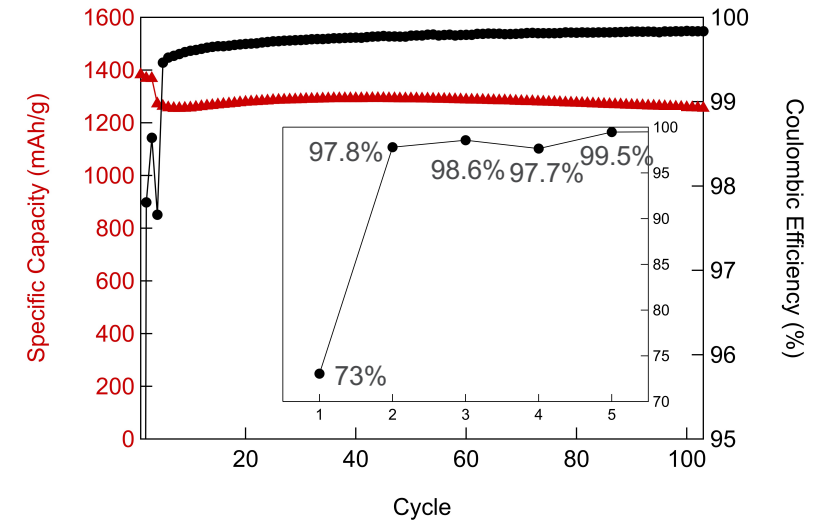
- Formation @ C/20 in half cell configuration (10-750 mV vs. Li)
- ~1.8 mAh/cm² LFP cathode
- ~0.6 mAh/cm² anode
- Formation @ C/20 in half cell configuration
- 5x @ C/3, 1x HPPC, 95x @ 1C, repeat (2.45-3.45V)

Half cell

Si@Li acrylate
5x @ C/20, cycled @
C/3, repeat (0.01-1.5V)

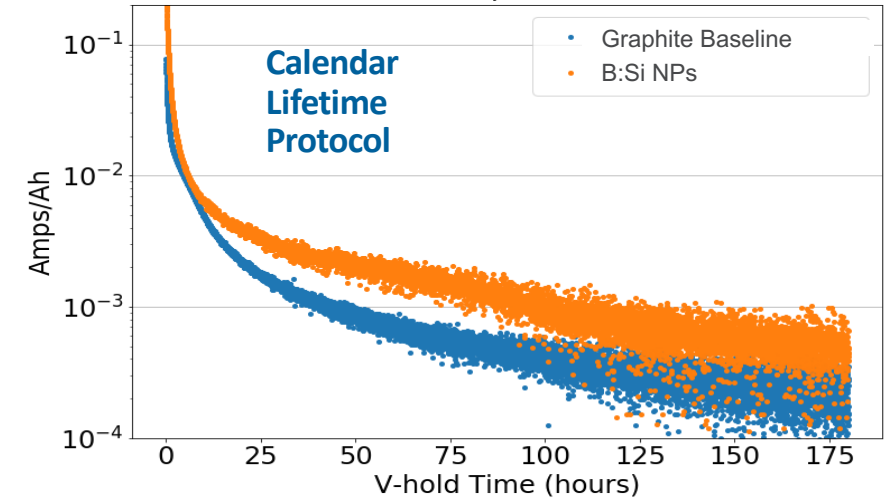
Target Metrics

> 1000 mAh/g
> 1000 mAh/cm³
> 3 mAh/cm²
> 99.98% CE
< 1.826*10⁻⁵
Amps/Ah
Li-consumption



Full cell

Si@Li₂CO₃
~0.6 mAh/cm² @ BOL
vs ~1.8 mAh/cm² LFP
~90% capacity
retention at cycle 500 (@ C/3)



Next Steps: 1. Understand early-cycle CE; 2. Understand porosity; 3. Increase areal capacity

SI@POLY(PMI) CONDUCTIVE COATING

Accomplishment

Electrode fabrication:

- Intrinsic 30 nm PECVD Si@SiH_x coated with polyphenylmethylimine (polyPMI)
- Slurry: 8 Si@polyPMI (3:1 Si:polyPMI) : 2 C65 in dyglyme
- 300 °C electrode cure to complete polymerization
- Cycling in Gen2 + 10% FEC Electrolyte

Full-cell cycling:

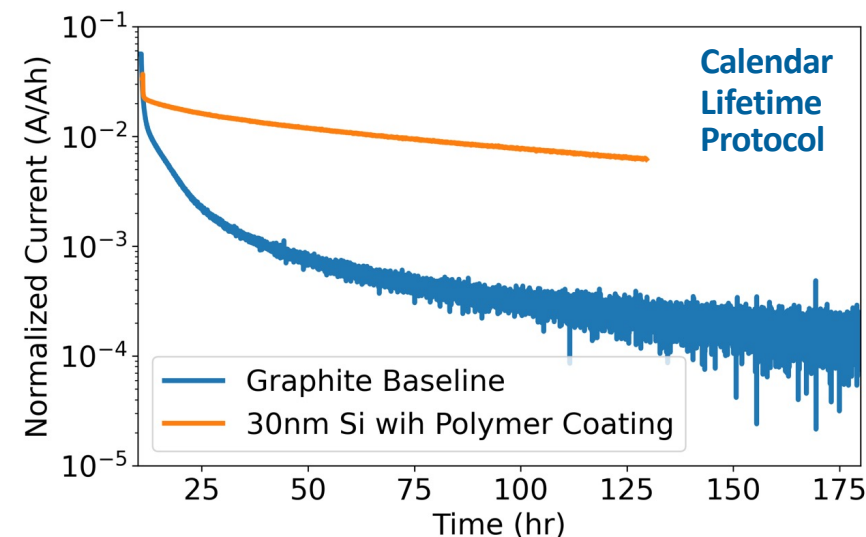
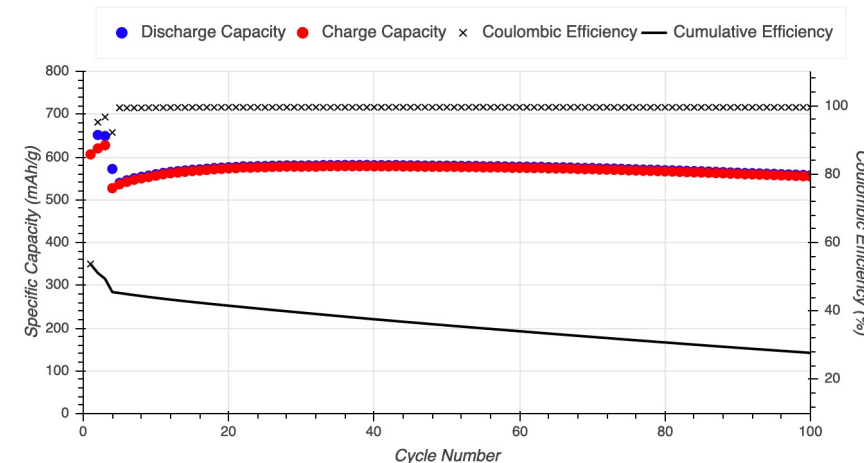
- No prelithiation
- ~1.8 mAh/cm² LFP cathode
- ~0.7 mAh/cm² Si (>150% excess Li-inventory)
- 4x @ C/3, 1x HPPC, 95x @ 1C, repeat (2.7-3.44V)

Half cell

3x @ C/20, 100x @ C/3 (0.01-0.75V)

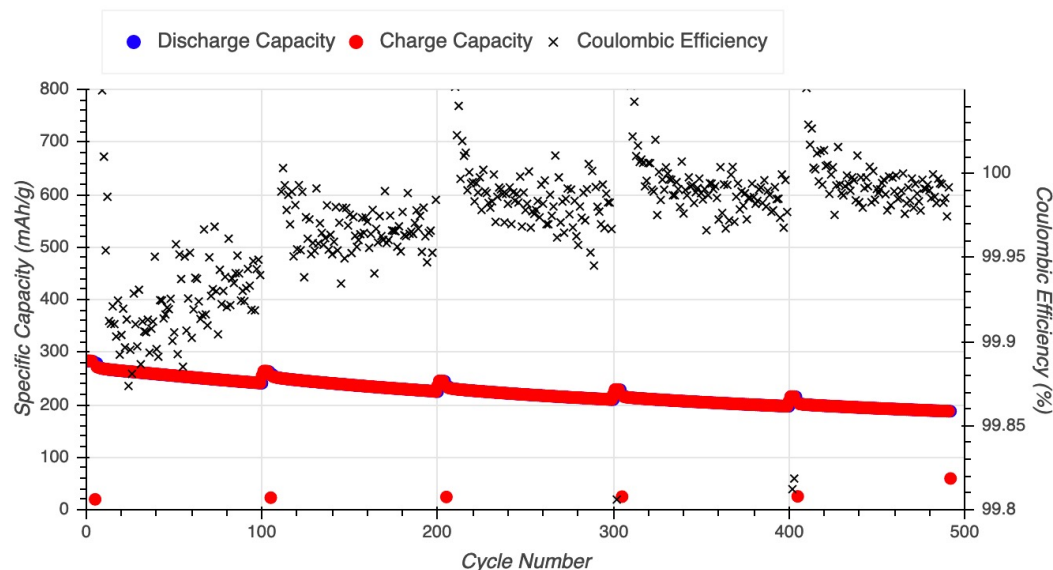
Target Metrics

> 1000 mAh/g
> 1000 mAh/cm³
> 3 mAh/cm²
> 99.98% CE
< 1.826*10⁻⁵ Amps/Ah
Li-consumption



Full cell

~0.7 mAh/cm² @ BOL
vs ~1.8 mAh/cm² LFP
~80% capacity retention at cycle 400 (C/3)



Next Steps: 1. Understand high CE; 2. Increase areal capacity; 3. Alternative coating methods

SUMMARY: INTERFACE ENGINEERED SI

Accomplishment

- Comparison of different interface engineered Si electrodes in the SCP

Target Metrics

> 1000 mAh/g
 > 1000 mAh/cm³
 > 3 mAh/cm²
 > 99.98% CE
 < 1.826*10⁻⁵
 Amps/Ah
 Li-consumption

| | CM Si@pitch | Osaka SiO | PECVD Si@NMP |
|---|------------------------------------|--|---|
| Electrode composition (Si:C45/C65:binder) | 90:10 Si@pitch:C45:P84 80:10:10 | SiO:C45:P84 70 : 10 : 20 | Si@NMP:C45:P84 30:45:15 |
| Electrolyte | Gen2 | Gen2 + 4 wt% FEC | Gen2 + 10 wt% FEC |
| Prelithiation (Y/N) | N | Y | Y |
| Specific stabilized capacity after forming in full-cell | N/A | 1000 mAh/g (C/10) | 500 mAh/g (C/3) |
| Stabilized Areal Loading (mAh/cm ²) | 0.47 | 1.3 (vs 1.5 mAh/cm ² NMC622) | 1.42 (vs 1.5 mAh/cm ² NMC622) |
| Cycle lifetime (1C; slower C-rate every 100 cycles) | N/A | 97% (C/10) at 300 cycles 88% (C/10) at 700 cycles | ~80% at 300 cycles (C/3) ~60% at 1000 cycles (C/3) |
| Terminal current (A/Ah) after 180 h @ 0.1 V vs LFP | N/A | N/A | Invalid test (Li-ion inventory consumed) |

SUMMARY: INTERFACE ENGINEERED SI

Accomplishment

- Comparison of different interface engineered Si electrodes in the SCP

Target Metrics

> 1000 mAh/g
> 1000 mAh/cm³
> 3 mAh/cm²
> 99.98% CE
< 1.826*10⁻⁵
Amps/Ah
Li-consumption

| | PECVD Si@pitch | PECVD B:Si@Li ₂ CO ₃ | PECVD Si@polyPMI |
|---|--|---|--|
| Electrode composition (Si:C45/C65:binder) | Si@pitch:C65:P84 8:1:1 | 11:2 Si@Li ₂ CO ₃ :CNTs:PAA 65:5:30 | SiO:C45:P84 70 : 10 : 20 |
| Electrolyte | Gen2 + 10 wt% FEC | Gen2 + 10 wt% FEC | Gen2 + 10 wt% FEC |
| Prelithiation (Y/N) | Y | Y | N |
| Specific stabilized capacity after forming in full-cell | 700 mAh/g (C/3) | 900 mAh/g (C/3) | 300 mAh/g (C/3) |
| Stabilized Areal Loading (mAh/cm ²) | 0.8 (vs 1.8 mAh/cm ² LFP) | 0.6 (vs 1.8 mAh/cm ² LFP) | 0.7 (vs 1.8 mAh/cm ² LFP) |
| Cycle lifetime | ~90% at 300 cycles (C/3) ~57% at 900 cycles (C/3) | ~86% at 300 cycles (C/3) ~90% at 500 cycles (C/3) | ~86% at 300 cycles (C/3) ~80% at 400 cycles (C/3) |
| Terminal current (A/Ah) after 180 h @ 0.1 V vs LFP | 3.9 x 10 ⁻⁴ | 4.5 x 10 ⁻⁴ | <3 x 10 ⁻³ |

CONCLUSIONS AND NEXT STEPS

Initial progress toward Q4 Milestones

- Terminal current at 0.1 V hold approaching graphite for several systems
- Si-Ti metallic glass synthesized, electrochemical properties under study
- Several systems already exceed Q4 Milestone “300 cycles with <20% capacity fade”

Next Steps

1. Electrolyte formulation strategies ramping up
 - Additives (multivalent, polymerizable, commercial)
 - Reduce FEC concentration to ≤ 0.28 M (≤ 3 wt%)
 - Non-carbonate electrolytes
2. Continue non-equilibrium synthesis of Si alloys and understand their EChem properties
3. Interface Engineering
 - Promising early results from several approaches
 - Challenges observed with higher loading anodes (and cathodes)
 - Understand the evolution of porosity and its relationship to mechanical stresses

Any proposed future work is subject to change based on funding levels

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BACKUP SLIDES

DESIGN AND FABRICATE POUCH CELLS WITH PRELITHIATED SILICON-BASED ELECTRODES

Procedure used for initial Osaka SiO trials

1. Select electrodes with capacities >1 mAh/cm²
2. Prelithiate SiO_x anodes versus lithium metal
 1. Punch out anodes to xx3450 size (14.1 cm²) and vacuum dry
 2. Cut out oversized lithium foil sheets
 3. Assemble half cell in large reusable SS cell fixture from ATD Program
 4. Use Gen2 electrolyte + 4 wt.% FEC in dry room
 5. Apply formation cycles:
 1. Lithiate to 10 mV
 2. Cycle 6x between 700 – 50 mV
 3. End on delithiation at 850 mV
 6. Harvest electrode in dry room, and rinse briefly (15 sec) with DMC
3. Use NMC electrode with capacity slightly less than SiO_x reversible capacity.
4. Quickly assemble in dry room with fresh Gen2 + 4 wt.% FEC
5. Cycle in capacity-limited mode to “break in” cathode
6. Perform abbreviated rate test (3x C/10, 3x C/3, 3x 1C, 3x 2C)
7. Life cycle test at 1C (3.0 - 4.15 V); C/10 every 100 cycles

